

NASA CR-132356

DEVELOPMENT OF A PROCESS FOR PRODUCING RIBBON SHAPED BORON FILAMENTS

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Prepared under Contract No. NAS 1-12125

by UNITED AIRCRAFT RESEARCH LABORATORIES
East Hartford, Connecticut 06108

for

NATIONAL AERONAUTIC AND SPACE ADMINISTRATION

(NASA-CR-132356) DEVELOPMENT OF A
PROCESS FOR PRODUCING RIBBON SHAPED BORON
FILAMENTS (United Aircraft Corp.) 38 37 p
HC \$4.00
CSC 13H

G3/15 24950

Unclass

N74-13201

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UNITS

Dimensional information is presented, in general, in the International System of Units (SI) with the equivalent values in the FPS system following in parenthesis.

All calculations were performed in FPS units and converted to SI units.

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DEVELOPMENT OF A PROCESS FOR
PRODUCING RIBBON SHAPED BORON FILAMENT*

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SUMMARY

The objective of this work was to produce a ribbon-shaped boron filament with a tensile strength of 138 KN/cm^2 (200 ksi). The investigation was carried out using both carbon and tungsten as substrate materials. No satisfactory results were obtained utilizing uncoated, copper-plated or silicon carbide coated tungsten ribbon substrates. Carbon ribbon substrates were prepared by pyrolysis of stretched polyimide tape. A severe deposition gradient occurred in all DC reactor experiments due to convective cooling at the edge of the substrate that resulted in a weak, non-uniform filament. RF heating, however, completely eliminated this gradient problem and a 90 cm (35.5") long boron ribbon was produced at .85 cm/sec (100 ft/hr) using a frequency of 40.68 megahertz. This boron ribbon, however, exhibited a light-bulb effect during deposition due to cracking of the deposit. Despite this effect, tensile strengths up to 59 KN/cm^2 (85.7 ksi) were obtained from this ribbon.

Several silicon carbide ribbon shaped filaments were also produced during this investigation by decomposition of $\text{CH}_3\text{SiHCl}_2$ onto carbon substrates. Contrary to the boron work, silicon carbide ribbon was readily prepared in DC static reactors. A very uniform and smooth deposition was obtained with strengths up to 71.1 KN/cm^2 (103.5 ksi).

*The contract research effort which has lead to the results of this report was financially supported by USAAMRDL (Langley Directorate).

INTRODUCTION

Most of the work conducted on high modulus composites recently developed for aerospace applications has involved the use of fibrous reinforcement. Considerable thought has been given to exploring the potential of tape-reinforced high modulus systems; but, unfortunately, no high-modulus, high-strength tape is available in quantities necessary to conduct meaningful composite studies. To date, studies which have been carried out have been only on model systems such as on glass tapes in resins and steel tape reinforced silver. The results of the model tape-reinforced composite studies have shown that higher transverse strengths and higher volume fractions of reinforcement could be attained in these composites than in those containing fibers. The shear strength should also be higher in tape-reinforced composites because of the increased surface of matrix bonding area and the compressive strength should be greater for the stiff tapes than it is for composites reinforced with carbon yarn composed of small flexible fibers. Because of these anticipated increased strengths, cross-ply and off-axis laminates may not be required in tape-reinforced structures.

The potential advantages of such tape reinforced structures led to this program directed towards producing a high modulus boron tape using both carbon and tungsten ribbon substrates.

METHOD OF APPROACH

Tungsten Substrate

Preliminary work at UARL prior to initiation of this program showed that reactions at the substrate interface could be either eliminated or drastically reduced by use of a diffusion barrier coating such as copper or silicon carbide. Therefore all tungsten ribbon substrate material was first coated with either copper or silicon carbide prior to boron deposition experiments.

Carbon Substrates

Another approach was that of using a substrate other than tungsten. The most logical choice was carbon since it has a low density, will not react with boron at deposition temperatures and has the potential of being a low cost substrate material. Several carbon tapes produced at UARL were used on this program.

Tungsten Ribbon Substrate

Experiments were conducted on bare tungsten ribbon as well as on SiC coated tungsten ribbon with various $H_2:BCl_3$ gas ratios, reactor designs, heating rates and deposition temperatures. In all cases the bare tungsten substrate crinkled and twisted when the deposit thickness became greater than $25.4\mu (.001")$ and the silicon carbide coated tungsten showed only a slight improvement over the bare ribbon.

Attempts to produce an all crystalline boron ribbon at very high heating rates were unsuccessful due mainly to uneven heating of the tungsten and burn out of the tungsten substrate.

Several pieces of tungsten ribbon were electroplated with copper of thicknesses from $2.5\mu (.0001")$ to $12.5\mu (.0005")$. A copper cyanide bath was used in a special plating jig that resulted in excellent uniformity along each piece.

The copper plated samples showed only a slight improvement over the bare tungsten substrate material. Kinks and curls still developed in the ribbon when the deposition thickness was over $25.4\mu (.001")$. A great deal of difficulty was also experienced using the copper plated samples in that it was almost impossible to keep the mercury in the electrodes due to its wetting the copper plated surface of the ribbon. Because of the lack of improvement in the deposition and the trouble with the seals the copper plating was abandoned as not being practical while using mercury seal electrodes.

Carbon Ribbon Substrate

Preliminary experiments in a DC reactor revealed a severe problem with the edges of the substrate tape. When heating the tape in the reactor, the edges of the tape remained dark even though the center of the tape was well into the red range of temperature. At the upper limits of the red range, the whole width of the tape was colored, but the difference between the center and edge temperature was still visually discernable. Heavy deposition occurred in the center of the width of the tape with little or no deposition at the edges. Experiments were conducted with various $H_2:BCl_3$ gas ratios and reactor geometries in attempts to overcome the edge effect. Gas ratios of H_2/BCl_3 were varied from 1:10 to 4:1, but varying the gas ratio did not radically change the deposition at the edges. Tape was precoated with a thin layer of SiC but this precoated tape did not produce any improvement in the boron tape.

It is felt that an uneven deposition caused by the temperature gradient across the tape was responsible for the crinkled edges, broken tape and spalling evident in tapes produced from these experiments. See Figures 1, 2 and 3.

Prior experiments on production of boron filament had shown that a pyrolytic graphite precoat on the substrate was necessary to prevent distortion or substrate fracture due to boron growth during deposition. This approach was also followed in experiments conducted under this program.

SUBSTRATE SELECTION OR PREPARATION

Tungsten

Tungsten ribbon, 12.5μ (.0005") thick x 2540μ (.10") was used for all tungsten substrate experiments. Since this material was received from the vendor in random lengths, from approximately 20 cm (8") to 30.5 cm (12") only static runs were performed. A second lot of tungsten ribbon was received in approximately 16M (50 ft) lengths that measured approximately 15.2μ (.0006") thick x 2540μ (.10") wide, since the vendor could not supply long lengths below the 15.2μ (.0006") thickness. This material was intended for use with a continuous process but was also used for copper diffusion barrier experiments since pieces longer than 20-25 cm (8-10") were required in the plating apparatus.

Carbon

The starting material for the preparation of all carbon substrate was Kapton^R polyimide ribbon. This material was slit to the desired width and then pyrolyzed in a three zone furnace to convert the ribbon to carbon. The carbon ribbon produced for use in the D.C. reactor experiments was 12.5μ (.0005") thick by 1250μ (.050") wide and tape used for the RF reactor experiments was approximately 12.5μ (.0005") thick by 200μ (.008") wide.

EXPERIMENTAL PROCEDURES AND RESULTS

Self Resistance Reactor Experiments

Several boron filament reactor electrodes were modified for use with ribbon substrates. These electrodes utilized mercury as both a sealing and electrical contact media. They worked well with the exception that mercury was vaporized at the top electrode when tungsten, particularly when copper plated, was heated. A water cooling coil around the electrode completely eliminated this problem.

All DC reactor runs were static with both tungsten and carbon substrates and heating was accomplished by means of self-resistance. Constant current DC supplies were used for the carbon substrates; constant voltage DC supplies were used for the tungsten substrates and a variable voltage AC supply was used for the copper plated tungsten experiments.

Mathematical calculations* indicated that the primary source of heat loss was due to convection currents. Three different reactor designs were used in attempts to disrupt the convection current and various gas flows were employed with each reactor design. First, a reactor was designed to produce turbulent flow within the reactor. Three back flow fins were inserted as shown, in Fig. 4. Secondly, a reactor was designed such that the gas flow through the reactor would approach static conditions as shown in Figs. 5 and 6. Thirdly, a thin, 7 mm (.28") diameter reactor with a short hot zone, 10 cm (4"); was used. Tape produced in these reactors was no better than that previously formed. Figure 7 is a tape produced in the turbulent reactor; the tape had a SiC precoating. Figure 8 is a tape produced in the turbulent reactor; the tape had no SiC precoat. Figures 9, 10, and 11 show tapes made in the static reactor. Figures 12 and 13 show tapes formed in the high velocity reactor.

The static reactor was then positioned so that the tape had its wide surface in a vertical direction. As was expected, the edge effect was changed. The deposit was shifted to the upper portion of the tape and a wider uncoated portion was at the bottom as shown in Figure 14.

In further attempts to eliminate convection cooling, experiments were conducted at reduced pressures. At a pressure of 24 mm (29" vacuum), with 400 cc/min gas flow and a 2:1 ratio of H_2 to BCl_3 , there was no visual edge effect and material was deposited over the entire surface of tape. The material was crystalline and the deposition rate was slow. Figures 15 and 16 show tapes produced at 20 and 30 minutes time at temperature. Deposits were also made at pressures of 250 mm and 506 mm (20 and 10" of vacuum). As the gas pressure increased, the edge effect increased, and an ionization phenomena occurred at reduced pressures whenever power was applied to or removed from the tape. This gas phenomenon and the slow deposition rate appear to make the low pressure deposition system impractical.

RF Heating

In order to ameliorate if not eliminate the edge cooling effects previously described several experiments were performed with carbon ribbon substrate utilizing RF heating. Because RF heating heats the edges of a thin ribbon higher than the center portion, it was felt that this could compensate for the unavoidable heat losses due to gas cooling.

Two different RF reactors were utilized for this work. Figure 17 shows the long continuous RF reactor (operating at a frequency of 40.68 megahertz) and Figure 18 shows the small static RF reactor (operating at a frequency of 150 megahertz) that were used for these experiments. Boron produced in the small static RF reactor did not produce very good boron tape but the deposit was uniform and very smooth. The major difficulty with this small rig was its low power rating. It could not maintain the ribbon at a constant temperature as the deposit thickness increased. It did however prove that a relatively uniform deposit was possible using RF heating.

*See Appendix

Two experiments were conducted using the long continuous reactor shown in Fig. 17. The substrate used for these experiments was $12\mu (.0047") \times 200\mu (.008")$ carbon that was precoated with pyrolytic graphite.

The H_2 to BCl_3 gas ratio was 2:1 with a total gas flow of 1200 cc/min. Substrate velocity was 0.17 cm/sec (20 ft/hr). Filament temperature was $1130^\circ C$. After a 15 second run, hot spots developed within the reaction and the tape separated. Figure 19 is a section of this tape and shows the uniform deposition obtained with an RF reactor.

The experiment was repeated at $1160^\circ C$ with a substrate velocity of .85 cm/sec (100 ft/hr). A 90 cm (35.5") testable length, $75\mu (.003") \times 175\mu (.007")$ was obtained even though "light-bulbing" took place. A fracture surface of this length is shown in Fig. 20 and the individual tensile tests are given in the following table:

Table of Individual Tensile Tests

Boron-Coated Carbon Tapes - RF Reactor

<u>KN/cm²</u>	<u>ksi</u>
29.6	42.9
16.4	23.8
34.5	50.0
59.0	85.7
55.0	80.0
56.8	82.4

No attempt was made during testing to pick specific areas so that some of the tests would have contained areas that light-bulbed and this could account for the variation in tensile values.

The light-bulbing phenomenon observed during boron deposition in the RF reactor was probably due to the fact that our carbon substrate had a relatively high modulus (approximately 12×10^6 N/cm² (17×10^6 psi)); the tensile strength of the substrate was therefore rapidly exceeded when the boron expansion took place and subsequent fracture of the substrate provided high resistance hot spots along the ribbon. A lower modulus carbon substrate with sufficient strength to prevent cracking should eliminate this problem. The high modulus substrate was produced using a highly stretched polyimide tape. Elimination of this stretching operation resulted in a tape that was not suitable for use as a substrate because of its excessive curvature, but somewhere between these two extremes may lie a set of conditions that will produce an ideal substrate for boron deposition. Deposition of boron on such a substrate in an RF reactor could produce a ribbon with the desired properties.

SiC Experiments

It was noted during the experiments involving a precoat of silicon carbide that its deposition on carbon substrate was much easier and more uniform than boron deposition. Since no great weight penalty would be paid by using SiC as opposed to boron several experiments were conducted to produce a silicon carbide ribbon. The DC static reactor previously used for boron deposition was utilized for these runs, and a 101μ (.004") x 178μ (.007") silicon carbide ribbon was obtained using methyl-dichlorsilane as a source gas. Figures 21 and 22 show cross-sections of two SiC ribbons obtained from these experiments. The deposition rate was at first so high that the reactor was not readily controlled and produced the ribbon shown in Fig. 21. This has a tensile strength of 37.6 KN/cm^2 (54.5 ksi). Reducing the amount of silane entering the reactor slowed down the deposition sufficiently to allow better control of the process and the ribbon shown in Fig. 22 was obtained. This material had a tensile strength of 71.4 KN/cm^2 (103.5 ksi). The uniformity of the deposit around the ribbon is very startling because of the complete absence of the gas cooling effect noted when depositing boron. Because of the ease of deposition it is felt that a continuous silicon carbide ribbon producing process could be readily achieved.

CONCLUSIONS

The production of high modulus ribbon material is feasible but particular attention must be paid to the method of heating and the state of the substrate material. Boron ribbon can be produced using RF heating of carbon substrate but the quality of the material produced will be very dependent upon the size (width) of the ribbon and its method of preparation.

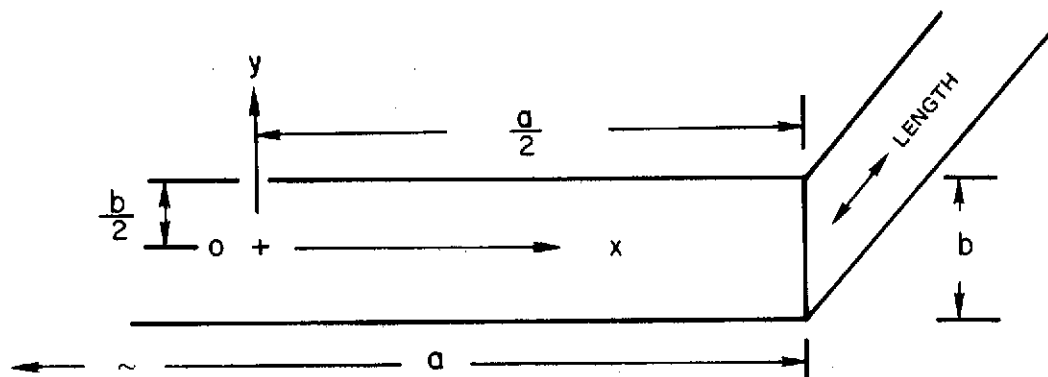
The use of RF heating solved the problem of nonuniform temperature distribution along the width of the ribbon for the size ribbon used for those experiments. The deposit was therefore uniformly distributed, even at the corners. However, since RF heating is well known to heat edges preferentially, there will be a limit on the maximum ribbon width at that point where the edge heating effect just balances the convective heat loss. At a width greater than this the edges will overheat and a dog-bone type ribbon should be obtained. This point, however may be at a relatively large width because of the high frequency at which the RF reactors operate. The maximum width usable with such reactors should be determined.

The uniformity and ease of deposition of silicon carbide using DC reactors leads to the conclusion that the decomposition rate of the silane compound utilized (methyl-dichlorosilane) is far less temperature sensitive than the hydrogen- BCl_3 reaction. The relatively high strength of the silicon carbide ribbon formed under this program should not by any means be taken as an upper value. The ribbon was formed under static substrate conditions and without benefit of parametric optimization. Normally a continuous reactor produces higher strength material than a static reactor and therefore silicon carbide ribbon produced in a continuous reactor should be a great deal stronger than that produced under this program.

APPENDIX

Heat Calculations

Heat calculations to determine the theoretical steady state heat loss of a ribbon to conduction were made as shown below:



$$k \frac{\partial^2 T}{\partial y^2} + G = 0$$

$$\frac{d^2 T}{dy^2} = - \frac{G}{K}$$

$$\frac{dT}{dy} = - \frac{Gy}{K} + C_1$$

$$T = - \frac{Gy^2}{2K} + C_1 y + C_2$$

a = WIDTH OF TAPE
 b = THICKNESS OF TAPE
 G = ENERGY GENERATION
 K = THERMAL CONDUCTIVITY
 T = TEMPERATURE
 h = COEFF. OF HEAT TRANSFER
 y = b DIRECTION
 x = a DIRECTION

in.
 in.
 $\text{cal/cm}^3 \text{sec}$
 $\text{cal/cm sec } ^\circ\text{C}$
 $^\circ\text{C}$
 $\text{cal/cm}^2 \text{sec } ^\circ\text{C}$

$$y = 0: \quad \frac{dT}{dy} = 0 = - \frac{G \cdot 0}{K} + C_1 \rightarrow C_1 = 0$$

$$y = \frac{b}{2}: \quad - \frac{dT}{dy} = \frac{h}{K} (T - T_{\text{amb}})$$

$$+ \frac{Gb}{2K} = \frac{h}{K} (T - T_{\text{amb}})$$

$$Gb = + 2h (T - T_{\text{amb}})$$

$$G = + \frac{2h}{b} (T - T_{\text{amb}})$$

$$\begin{aligned}\text{VOL HEATED} &= 4^{\text{IN.}} \times .08^{\text{IN.}} \times .0005^{\text{IN.}} \\ &= 10 \times .2 \times .0012 \text{ cm}^3 \\ &= .0024 \text{ cm}^3\end{aligned}$$

$$\text{SURFACE AREA} = 10 \times .2 \times 2 \text{ SIDES} = 4 \text{ cm}^2$$

$$G = \frac{\text{POWER}}{\text{VOL}} = \frac{100 \text{ watts}}{.0024 \text{ cm}^3} = \frac{100}{(4.18)(.0024)} \frac{\text{cal}}{\text{cm}^3 \cdot \text{sec}} = 10^4$$

$$h(T - T_{\text{amb}}) = \frac{Gb}{2} = \frac{10^4(.0012)}{2} = 6 \text{ cal cm}^2 \cdot \text{sec}$$

$$K = .06 \text{ cal cm} \cdot \text{sec} \cdot ^\circ\text{C}$$

$$T_{\text{surface}} = - \frac{10^4 \left(\frac{b}{2}\right)^2}{2K} + C_2 = 1150^\circ\text{C}$$

$$-10^4 \frac{b^2}{8K} + C_2 = -10^4 \frac{(1.44)10^{-6}}{8(.06)} + C_2 = 0.03 + C_2 = 1150$$

$$C_2 = 1150 \quad \Delta T = .03^\circ\text{C}$$

The results confirmed the intuitive conclusion that conduction across the tape played a minor role in producing the large temperature differences observed along the width of the filament since only a difference of 0.03°C is predicted.

The formula relating the parameters affecting convective heat transfer for a thin ribbon is shown below;

$$\bar{h} = 0.1K \left[\frac{\rho^2 g \beta \Delta T}{\mu^2 L} \left(\frac{C_{p\mu}}{K} \right) \right]^{0.25}$$

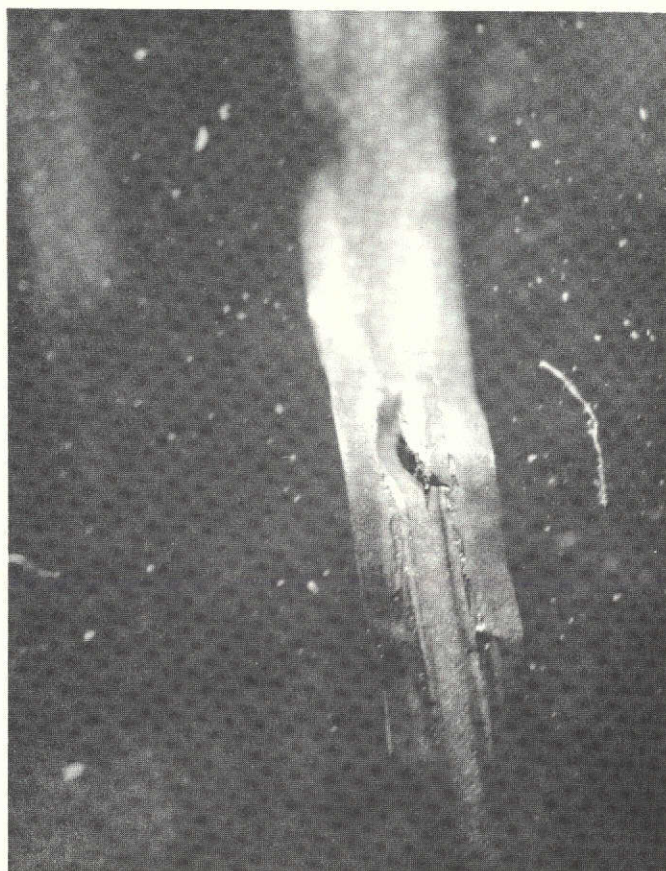
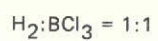
K	= thermal conductivity	cal/cm.sec.°C
ρ	= density	g/cm ³
g	= gravity	cm/sec ²
β	= coeff. of volumetric expansion	°C ⁻¹
ΔT	= temp. difference	°C
* μ	= viscosity	poise (f/cm.sec)
L	= length	cm
$\frac{C_{p\mu}}{K}$	= Prandtl No.	(dimensionless)
→	THEN $\frac{\dot{q}}{A} = h (T_{\text{surface}} - T_{\text{gas}})$	cal/sec
	where $\frac{\dot{q}}{A}$	= rate of heat transfer per unit area

*Note K & μ are approximately independent of pressure

Confirmation that this was the major mode of heat loss was obtained empirically during the low-pressure experiments. Decreasing the pressure in the vessel (decreases density) should, according to the formula, decrease the heat loss at the edges and this was confirmed during the experiments when a relatively uniform temperature across the piece was obtained at the lower pressures.

BORON-COATED CARBON TAPE

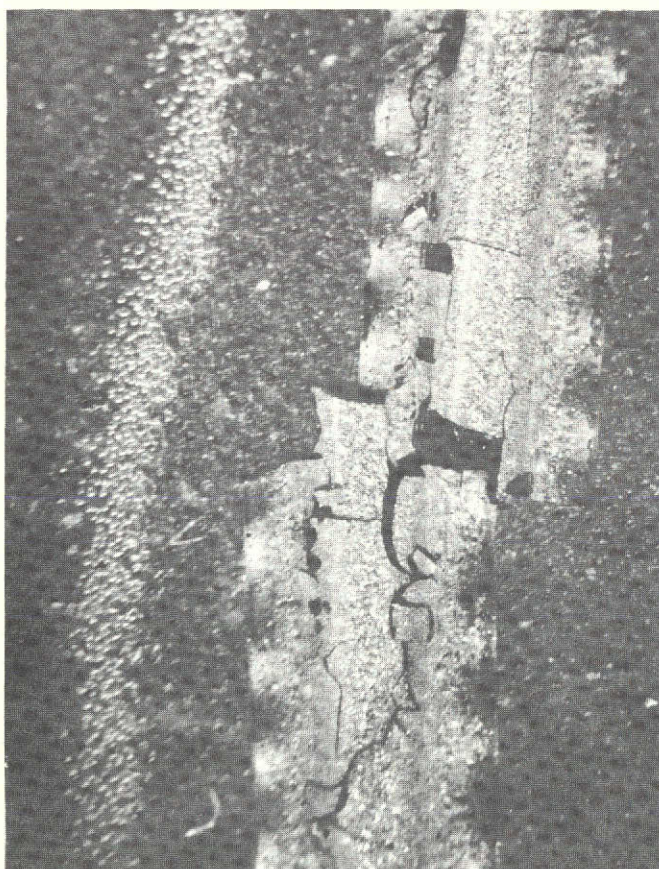
STANDARD REACTOR - NO PRECOAT ON TAPE

400 μ

BORON-COATED CARBON TAPE

STANDARD REACTOR — TAPE PRECOATED WITH SiC

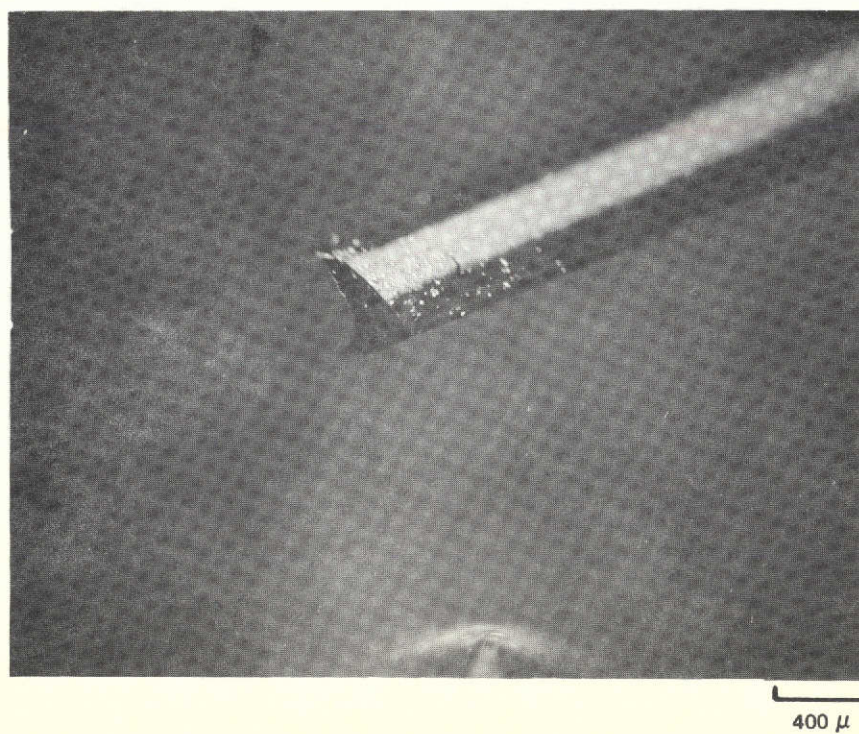
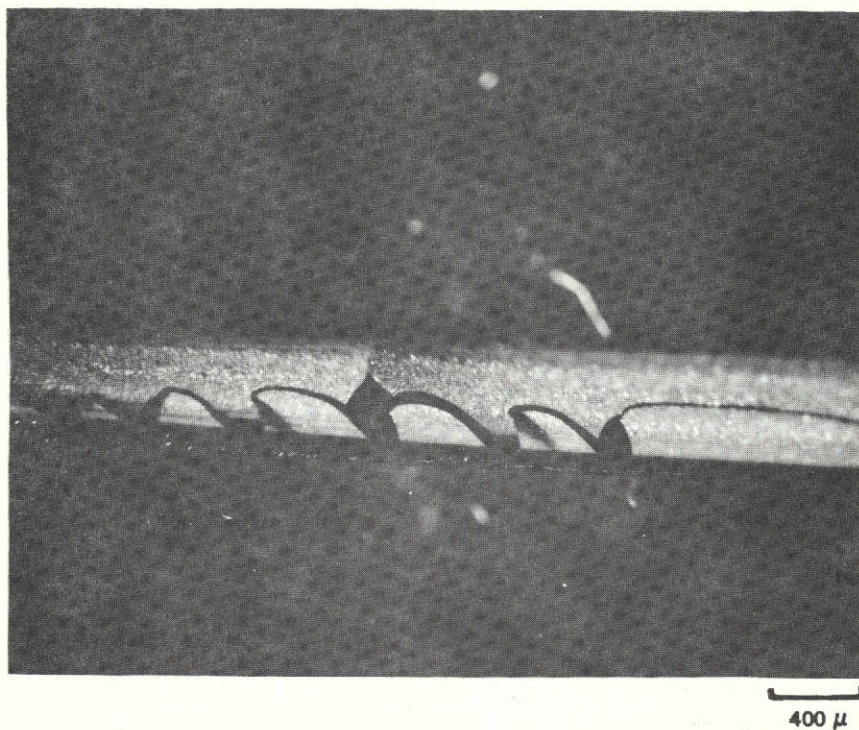
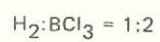
$\text{H}_2:\text{BCl}_3 = 1:1$



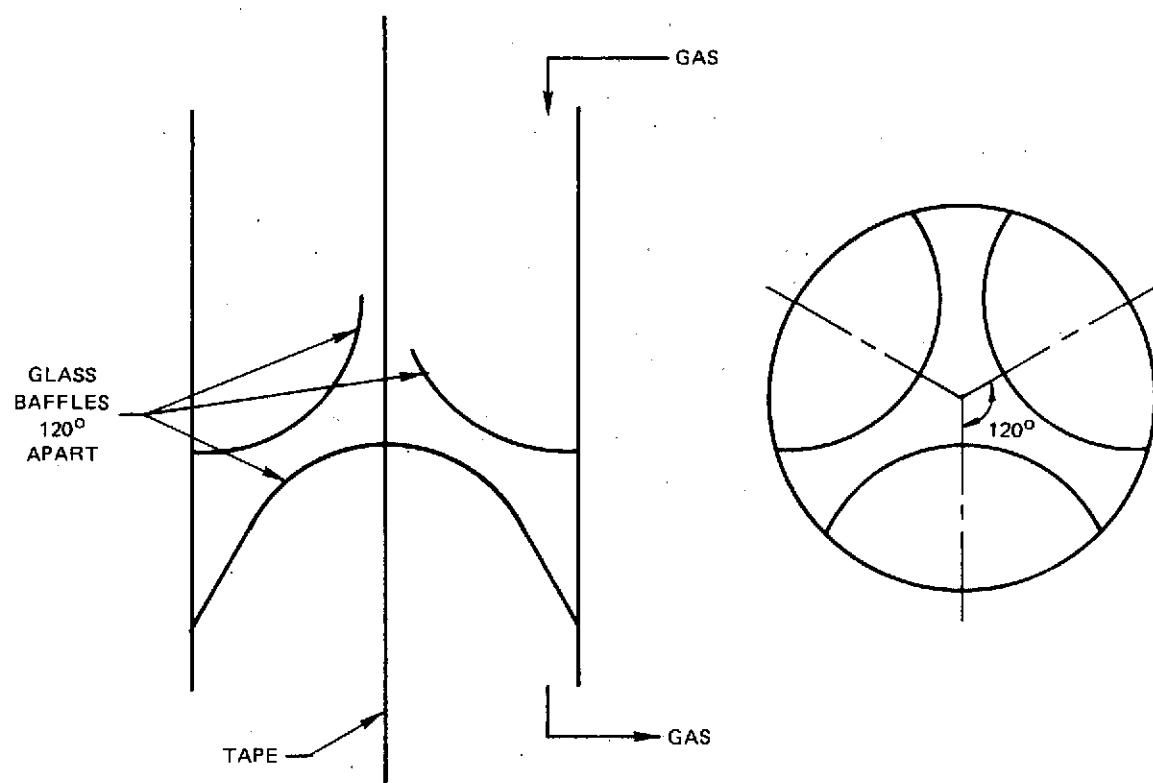
200 μ

BORON-COATED CARBON TAPE

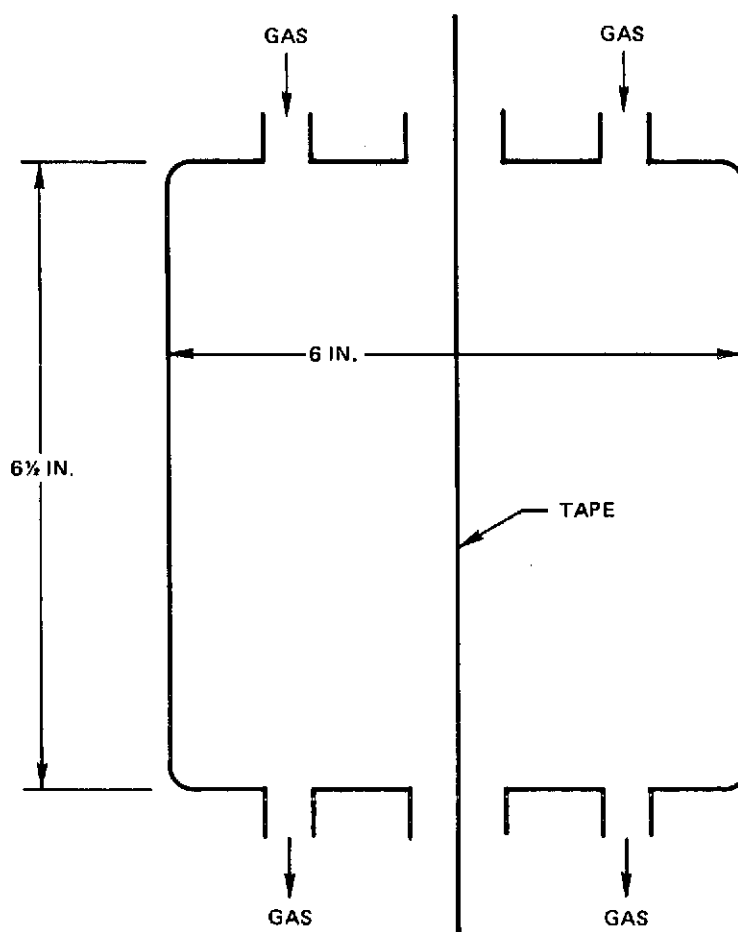
STANDARD REACTOR — TAPE PRECOATED WITH SiC

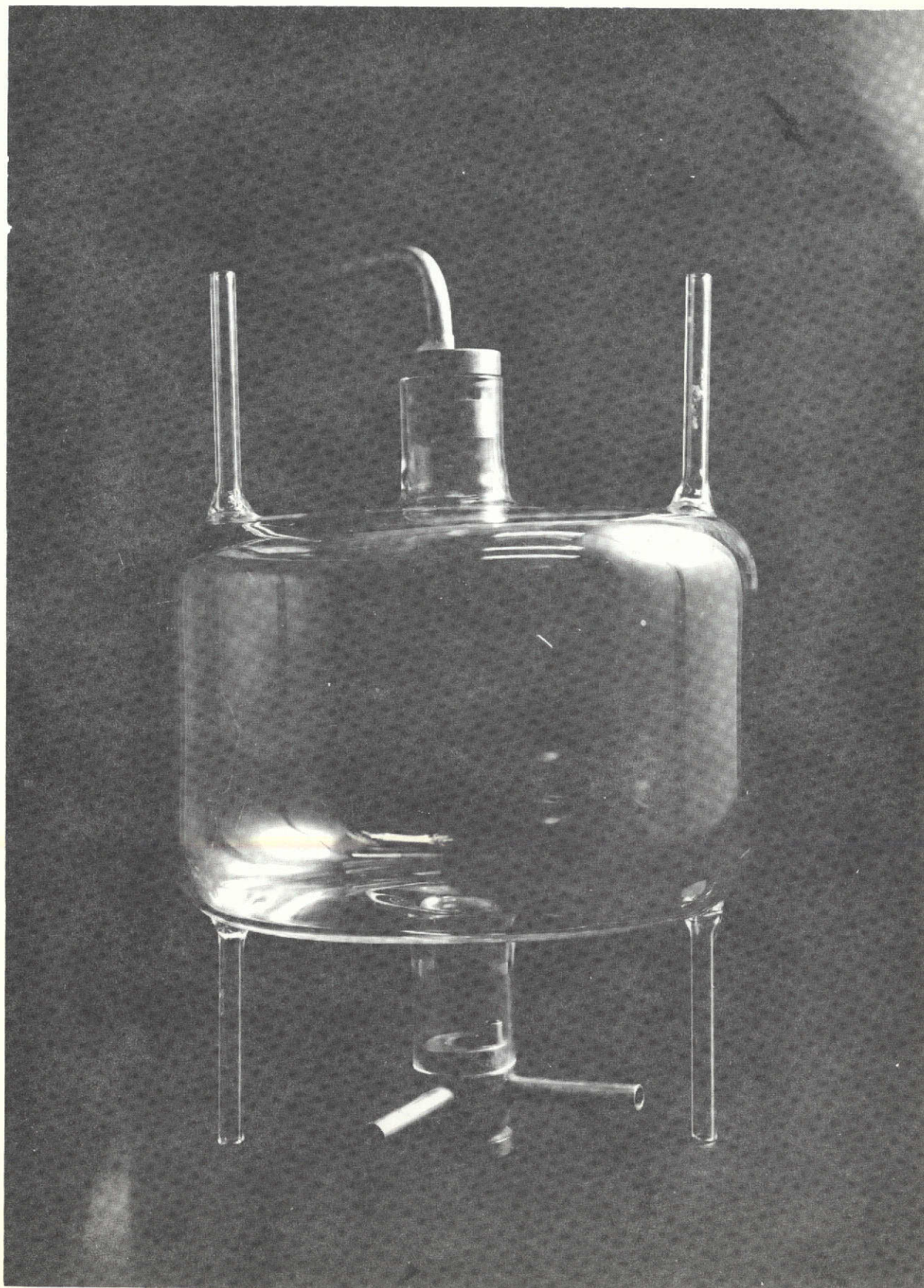


TURBULENT FLOW REACTOR



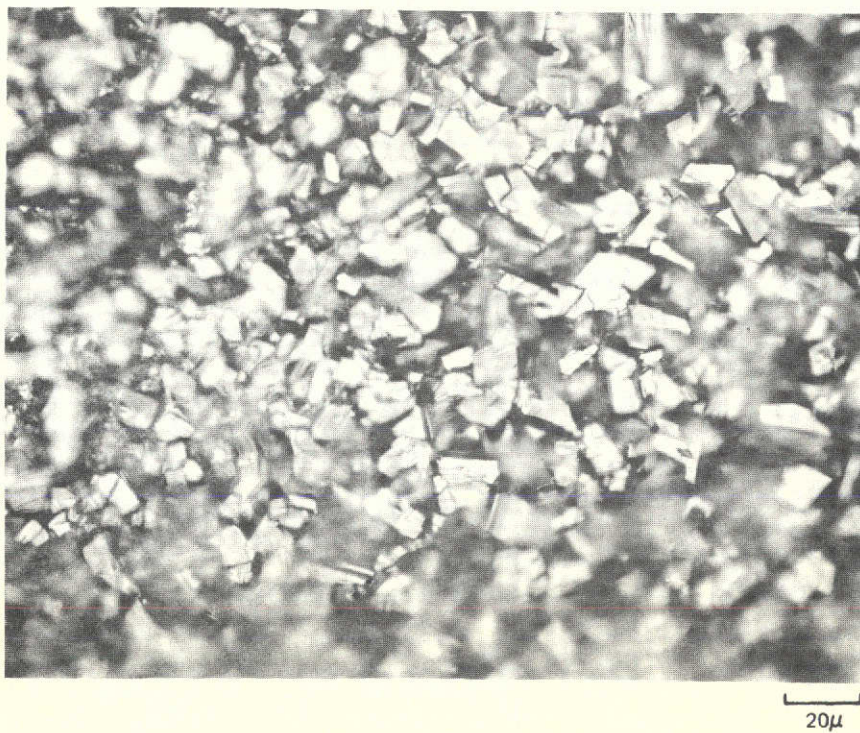
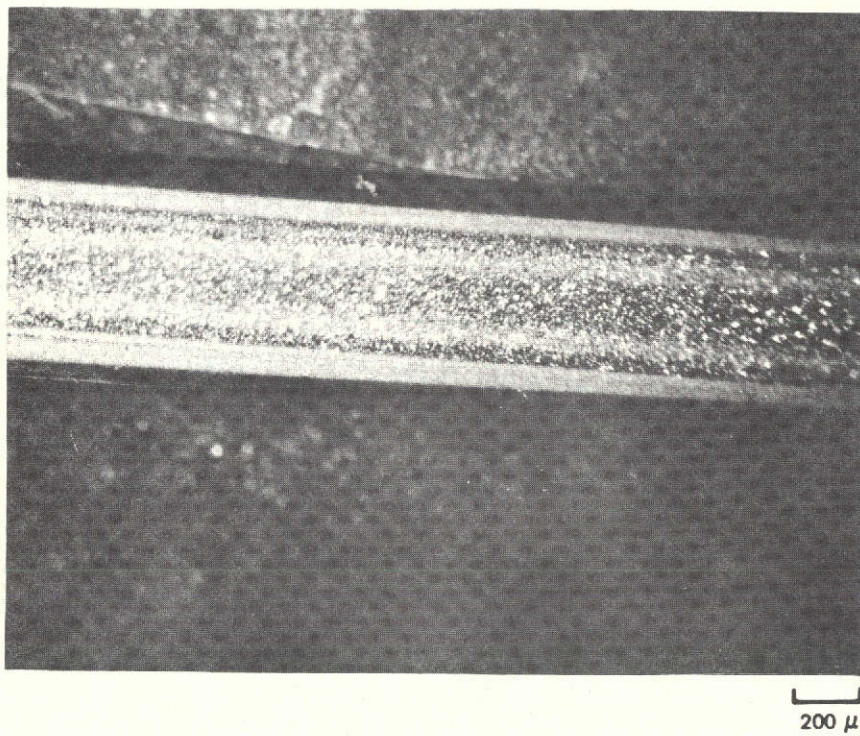
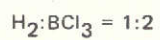
SCHEMATIC OF STATIC (LOW FLOW) REACTOR





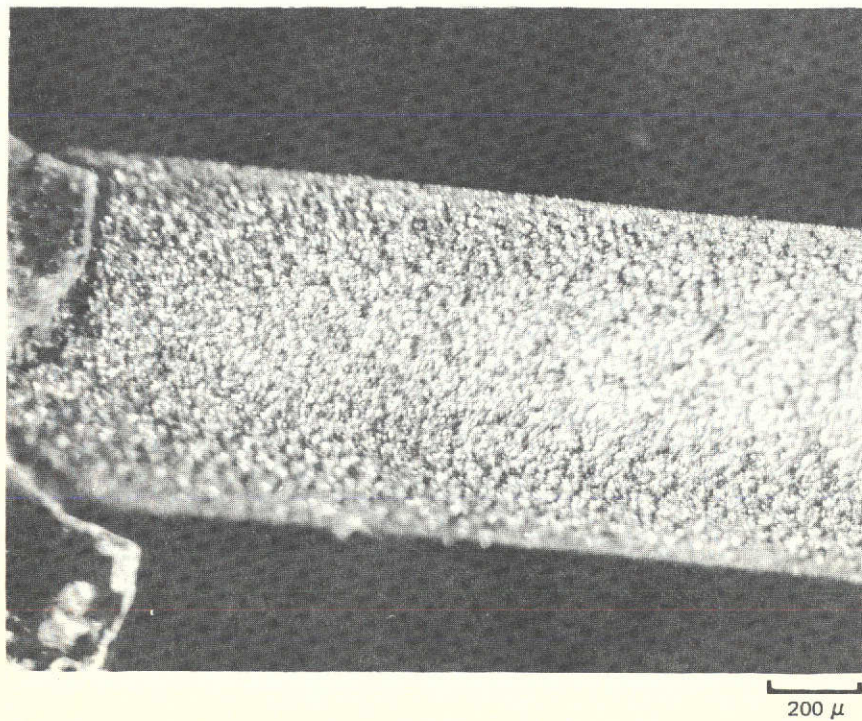
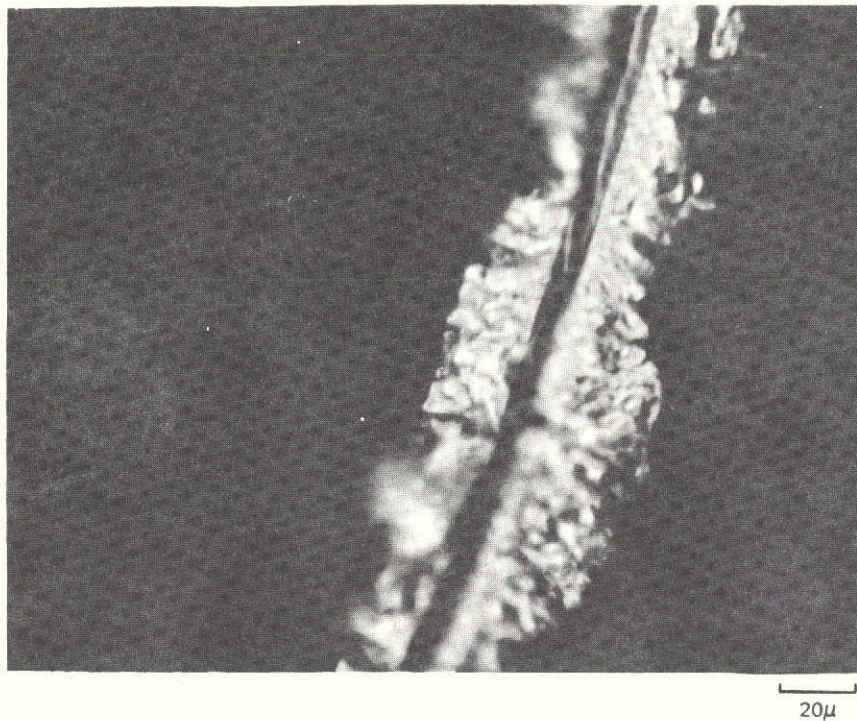
BORON-COATED CARBON TAPE

TURBULENT REACTOR - TAPE PRECOATED WITH SiC



BORON-COATED CARBON TAPE

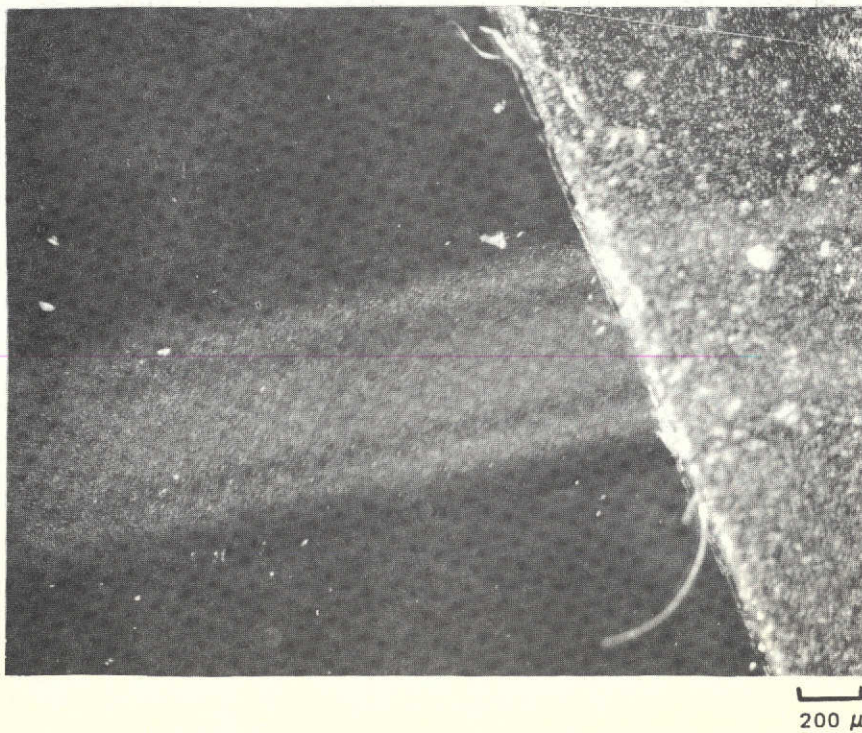
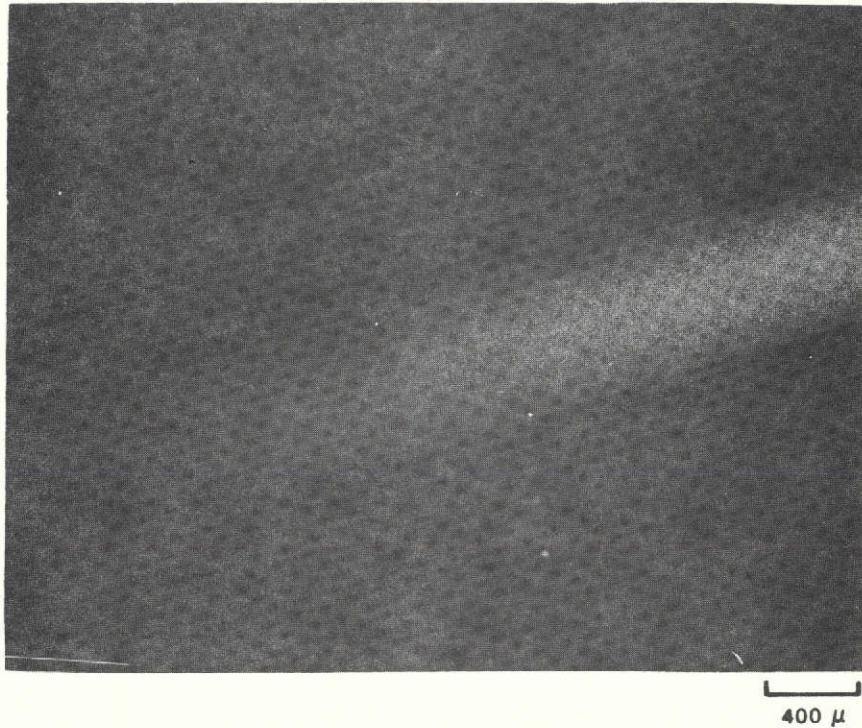
TURBULENT REACTOR — NO PRECOAT ON TAPE

 $H_2:BCl_3 = 1:10$ 

BORON-COATED CARBON TAPE

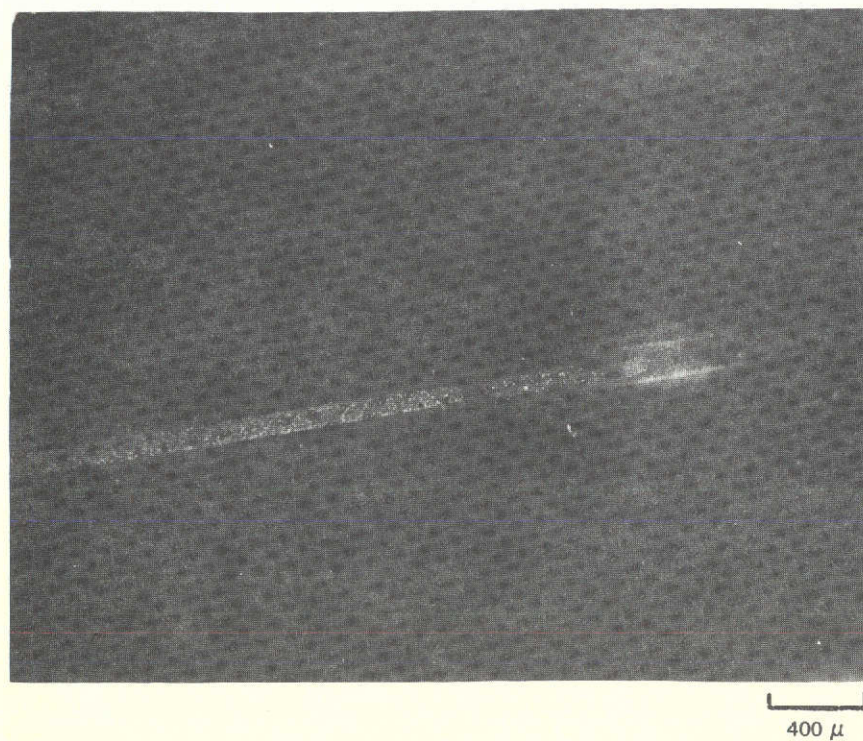
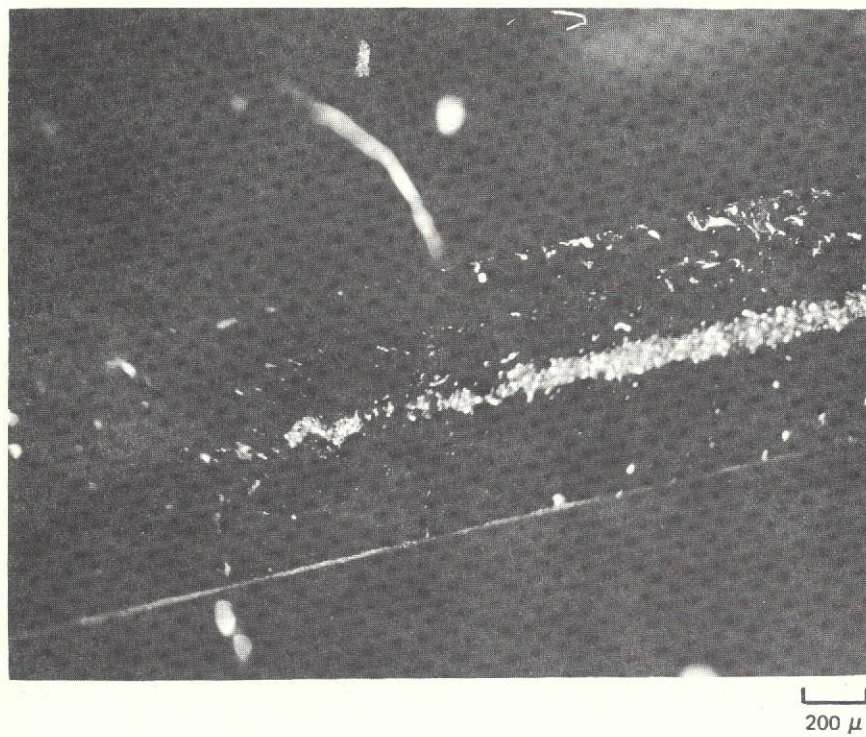
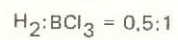
STATIC REACTOR — NO PRECOAT ON TAPE

$H_2:BCl_3 = 1:5$



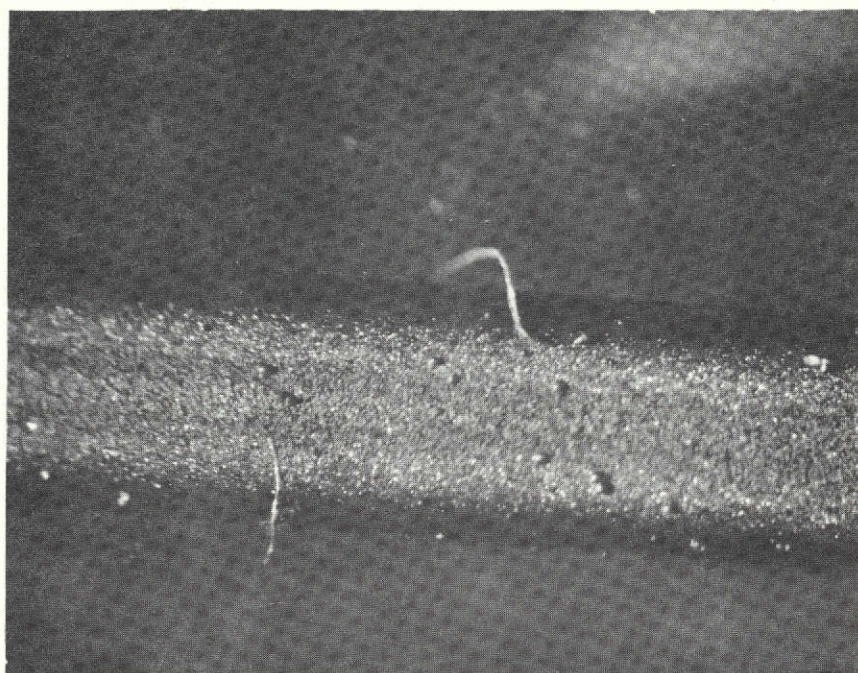
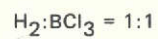
BORON-COATED CARBON TAPE

STATIC REACTOR - NO PRECOAT ON TAPE



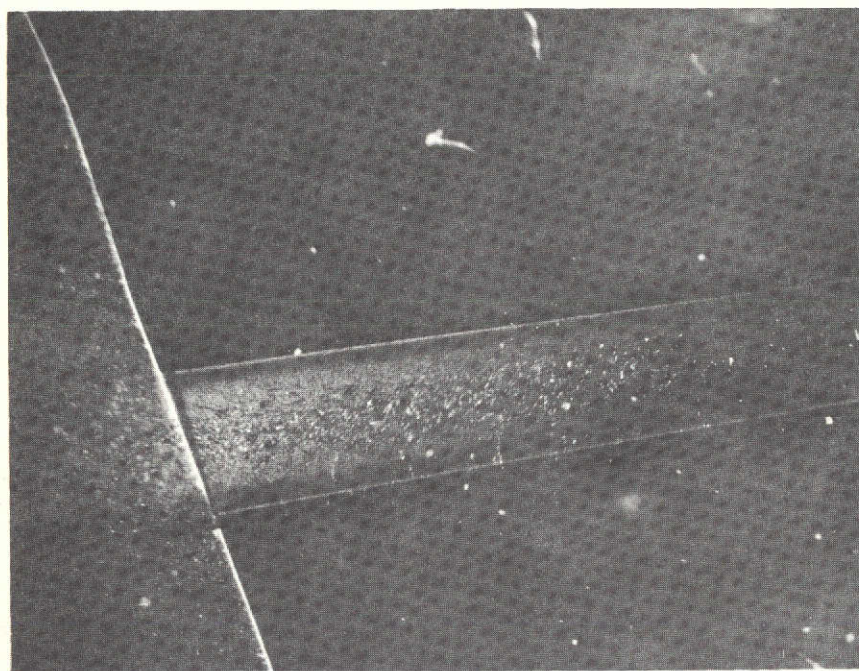
BORON-COATED CARBON TAPE

STATIC REACTOR — NO PRECOAT ON TAPE

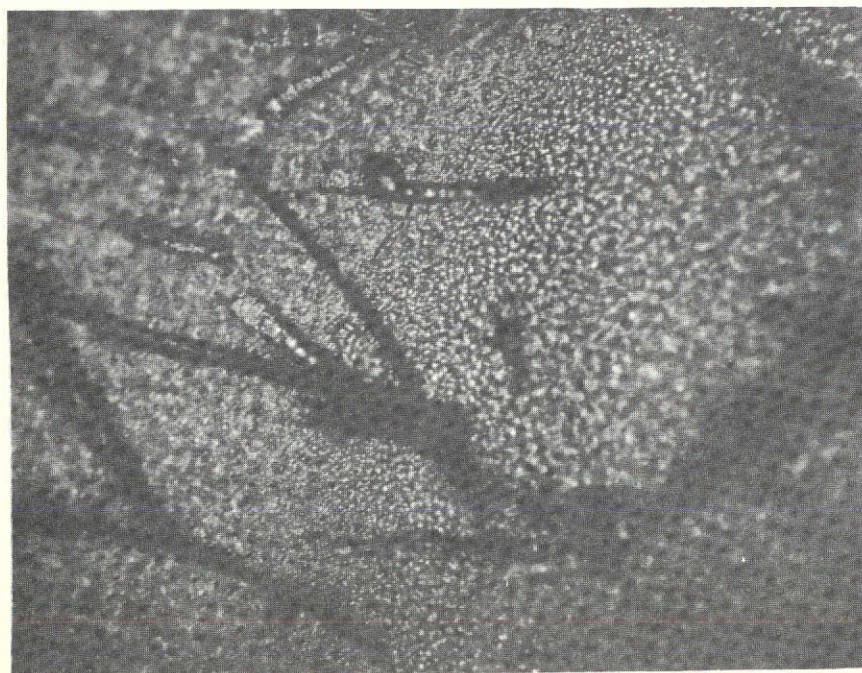
200 μ

BORON-COATED CARBON TAPE

HIGH VELOCITY REACTOR — NO PRECOAT ON TAPE

 $\text{H}_2:\text{BCl}_3 = 4:1$ 

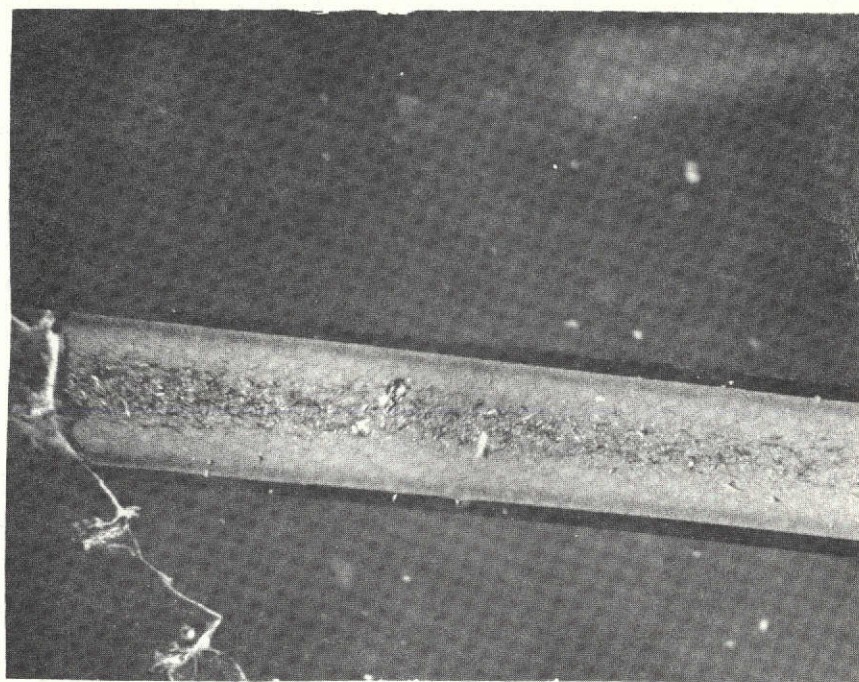
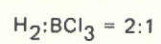
400 μ



20μ

BORON-COATED CARBON TAPE

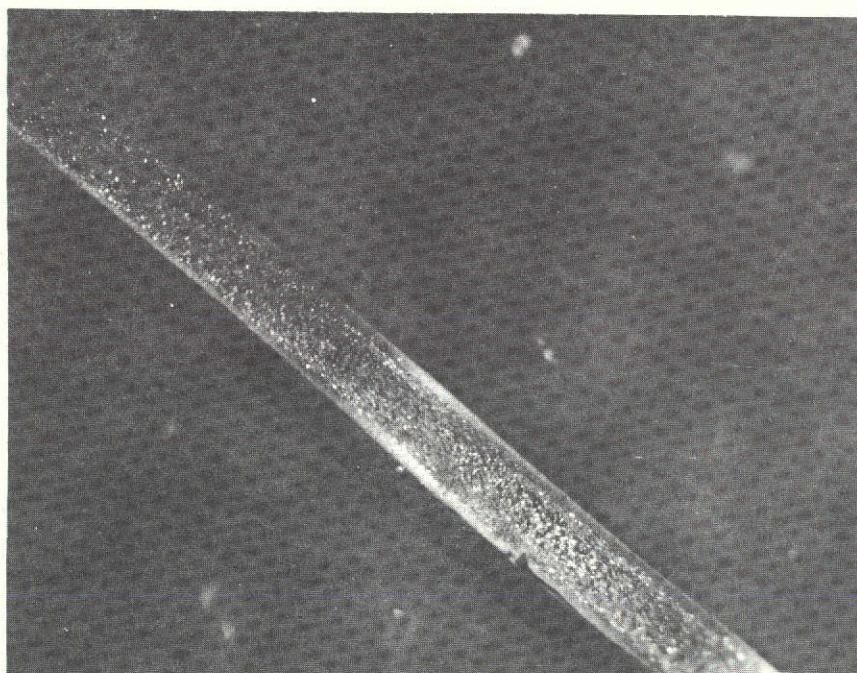
HIGH VELOCITY REACTOR – NO PRECOAT ON TAPE



400 μ

BORON-COATED CARBON TAPE

STATIC REACTOR — NO PRECOAT ON TAPE
WIDE SURFACE IN VERTICAL DIRECTION

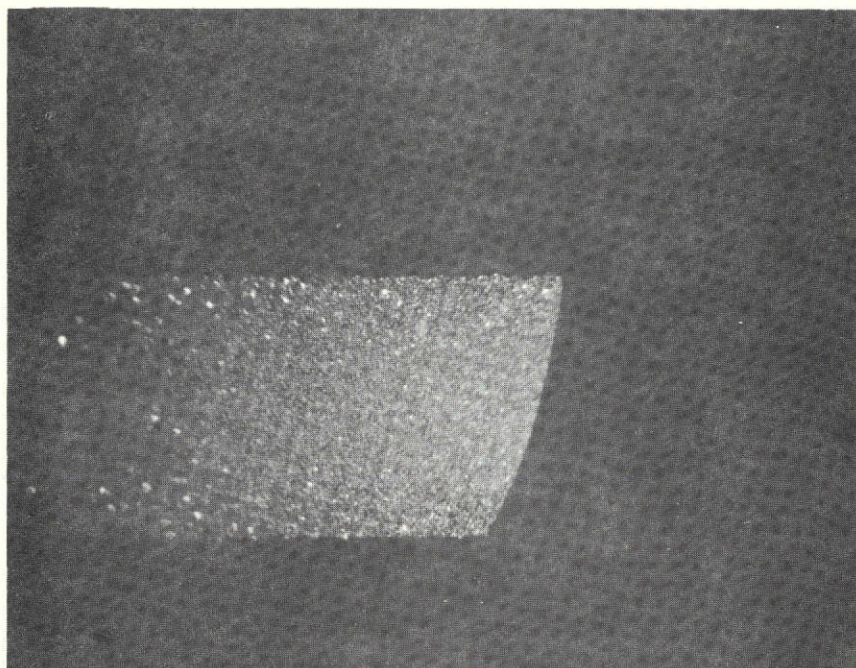


500 μ

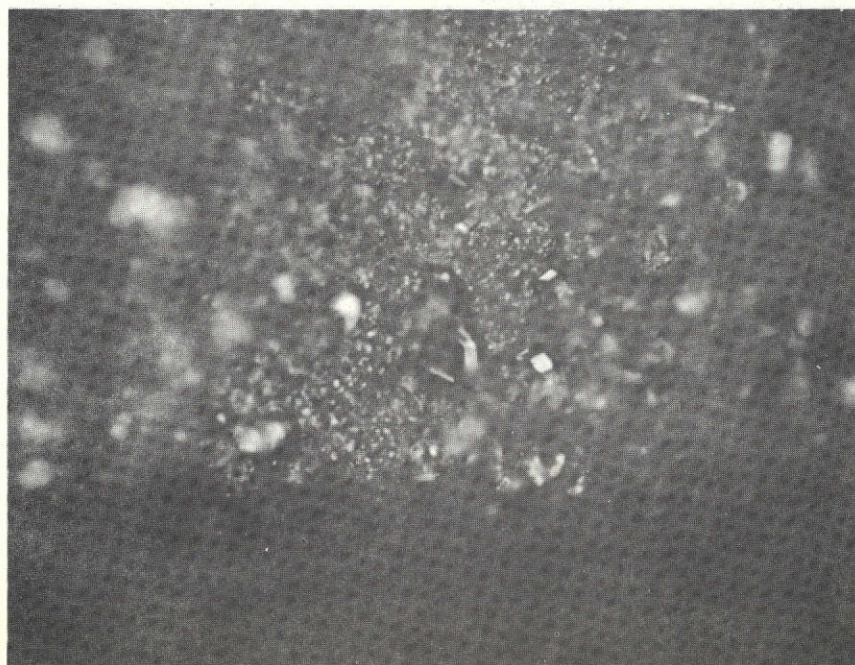
BORON-COATED CARBON TAPE

LOW PRESSURE REACTOR — NO PRECOAT ON TAPE

20 MIN DWELL

 $H_2:BCl_3 = 2:1$ 

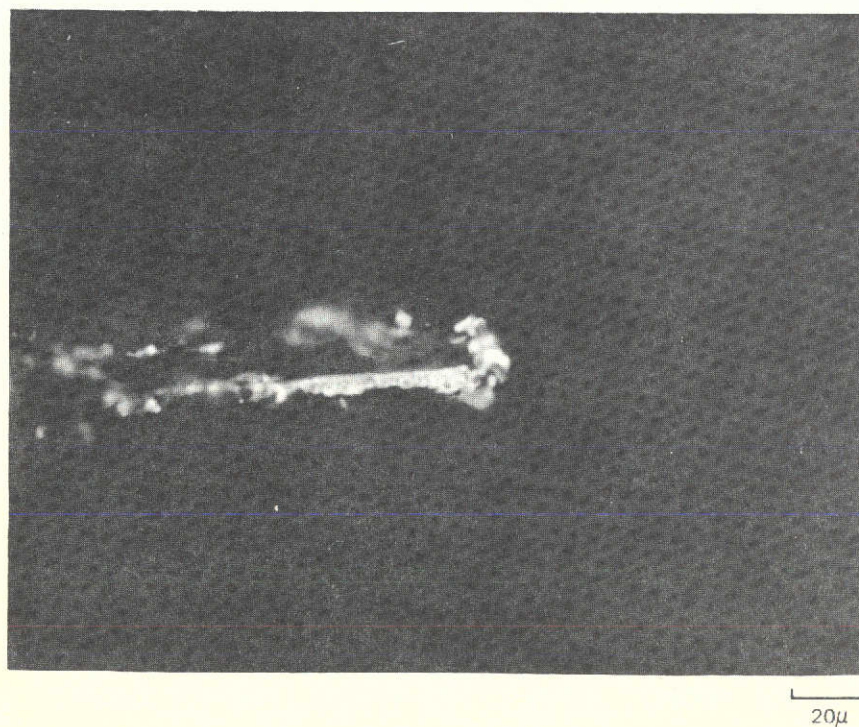
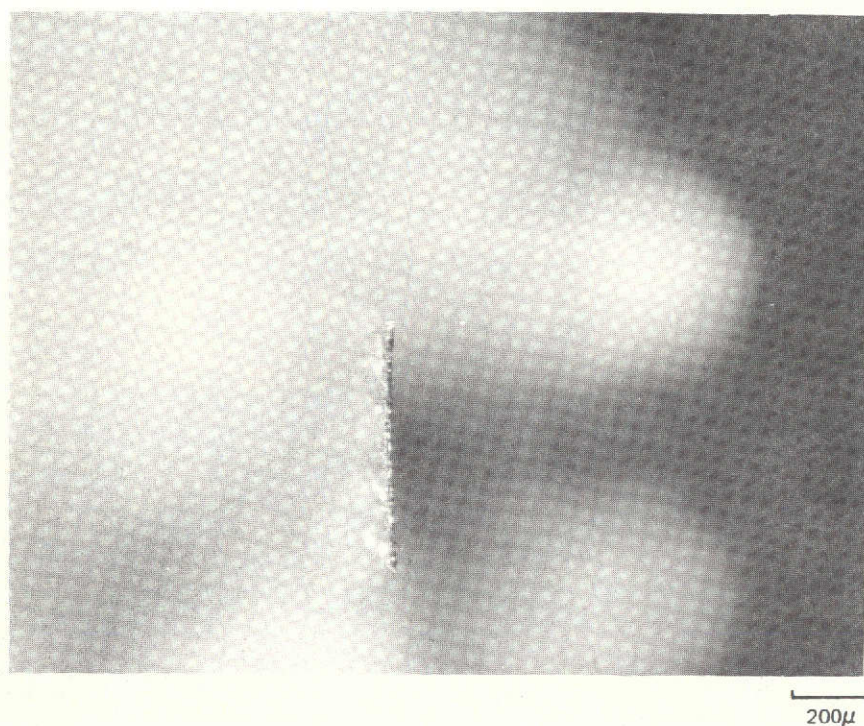
200μ



20μ

BORON-COATED CARBON TAPE

CROSS SECTION OF TAPE SHOWN IN FIGURE 15

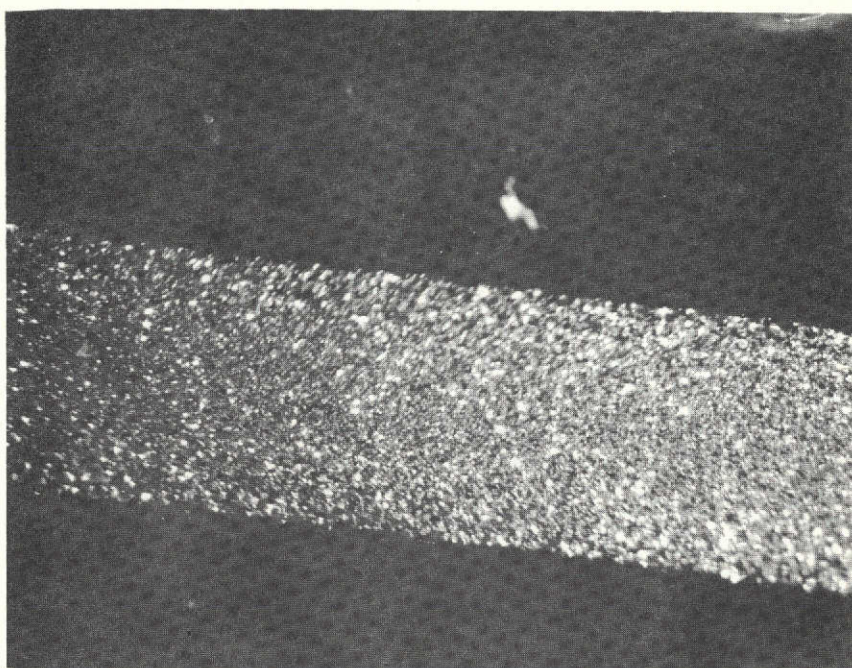


BORON-COATED CARBON TAPE

LOW PRESSURE REACTOR — NO PRECOAT ON TAPE

30 MIN DWELL

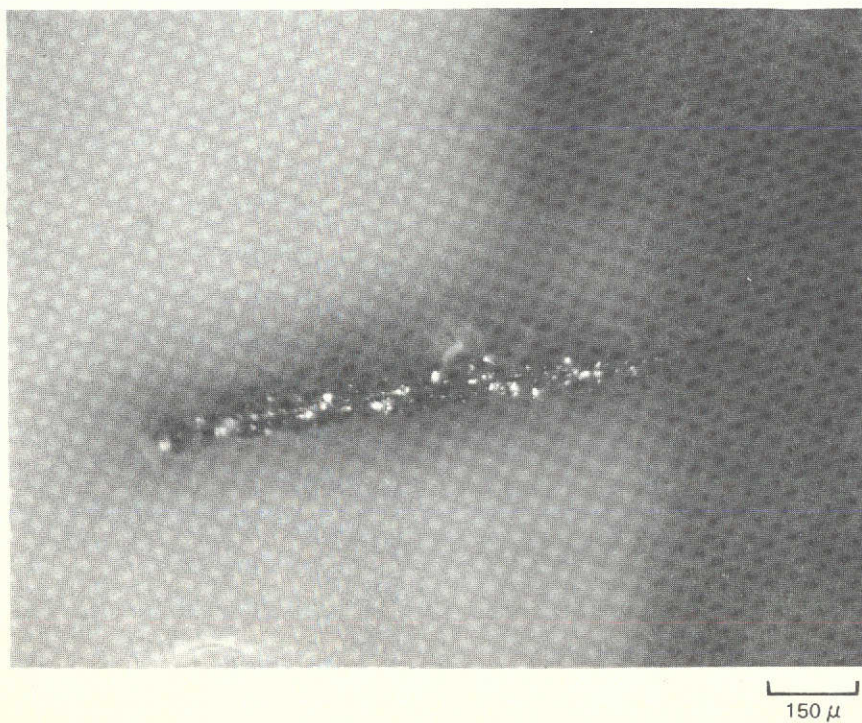
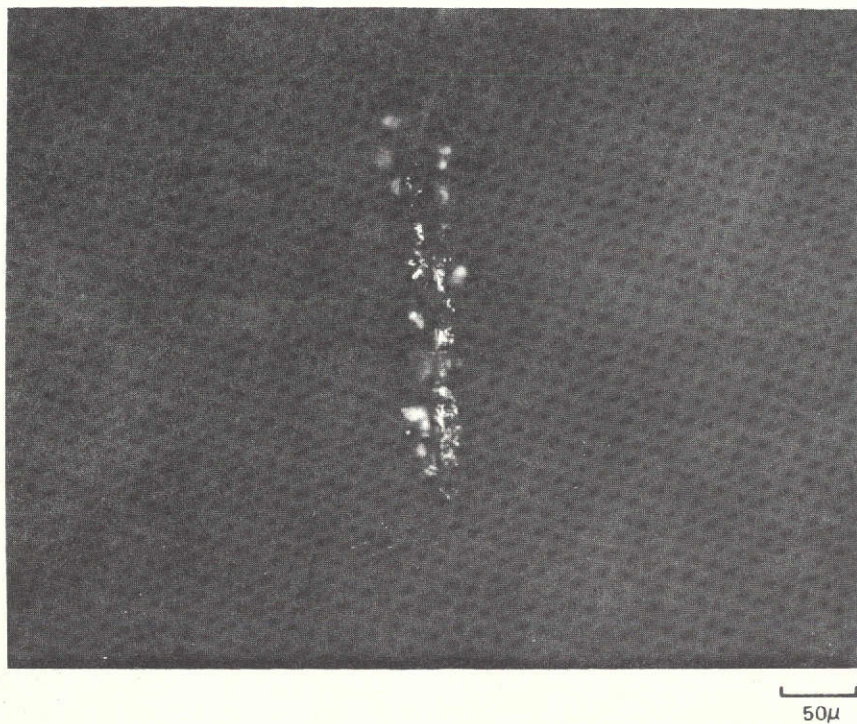
$H_2:BCl_3 = 2:1$



200 μ

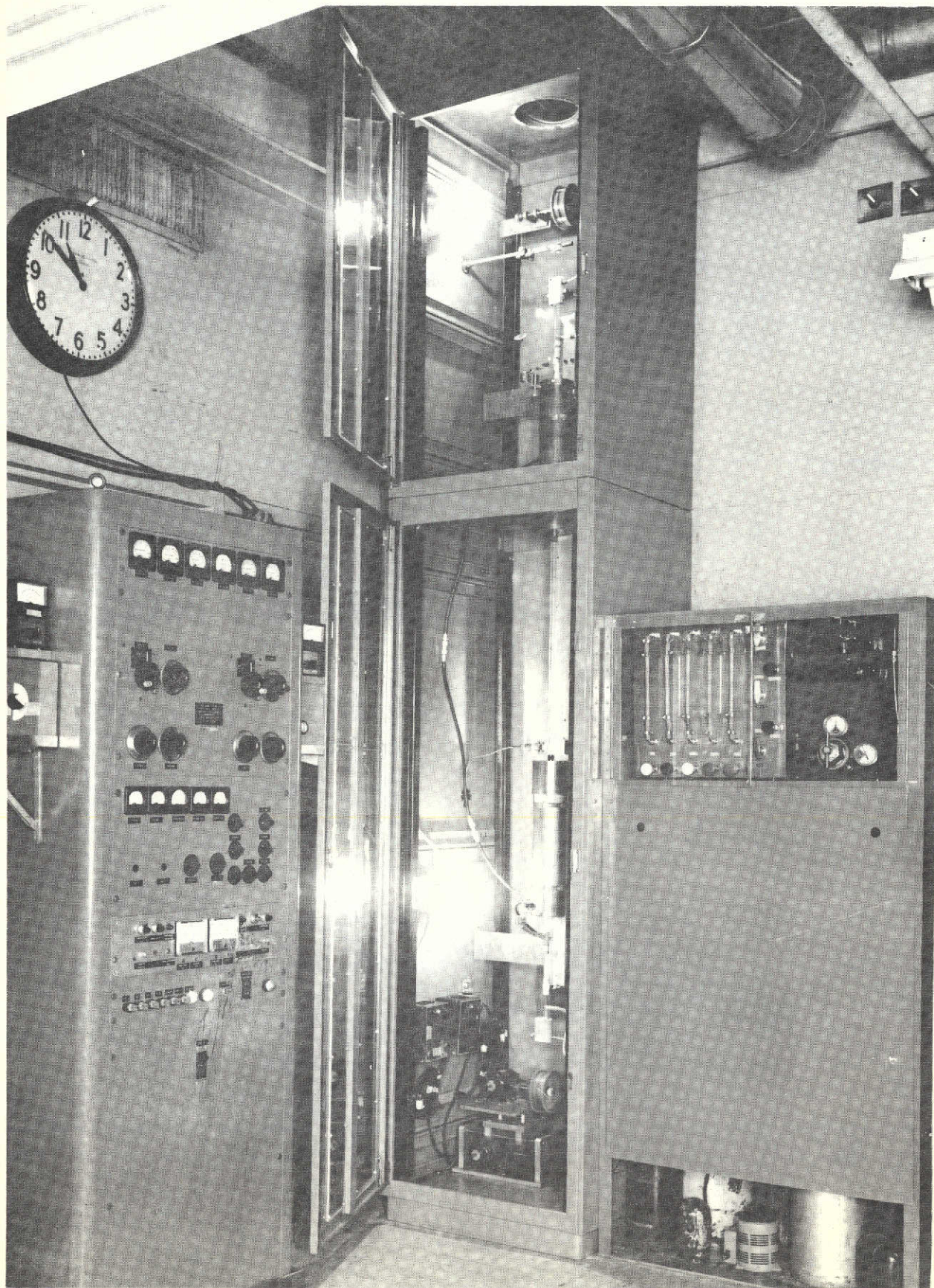
BORON-COATED CARBON TAPE

CROSS SECTION OF TAPE SHOWN IN FIGURE 16



CONTINUOUS RF REACTOR

OPERATING FREQUENCY — 40.68 MEGAHERTZ



RL-73-234-B

SMALL STATIC RF REACTOR
OPERATING FREQUENCY — 150 MEGAHERTZ

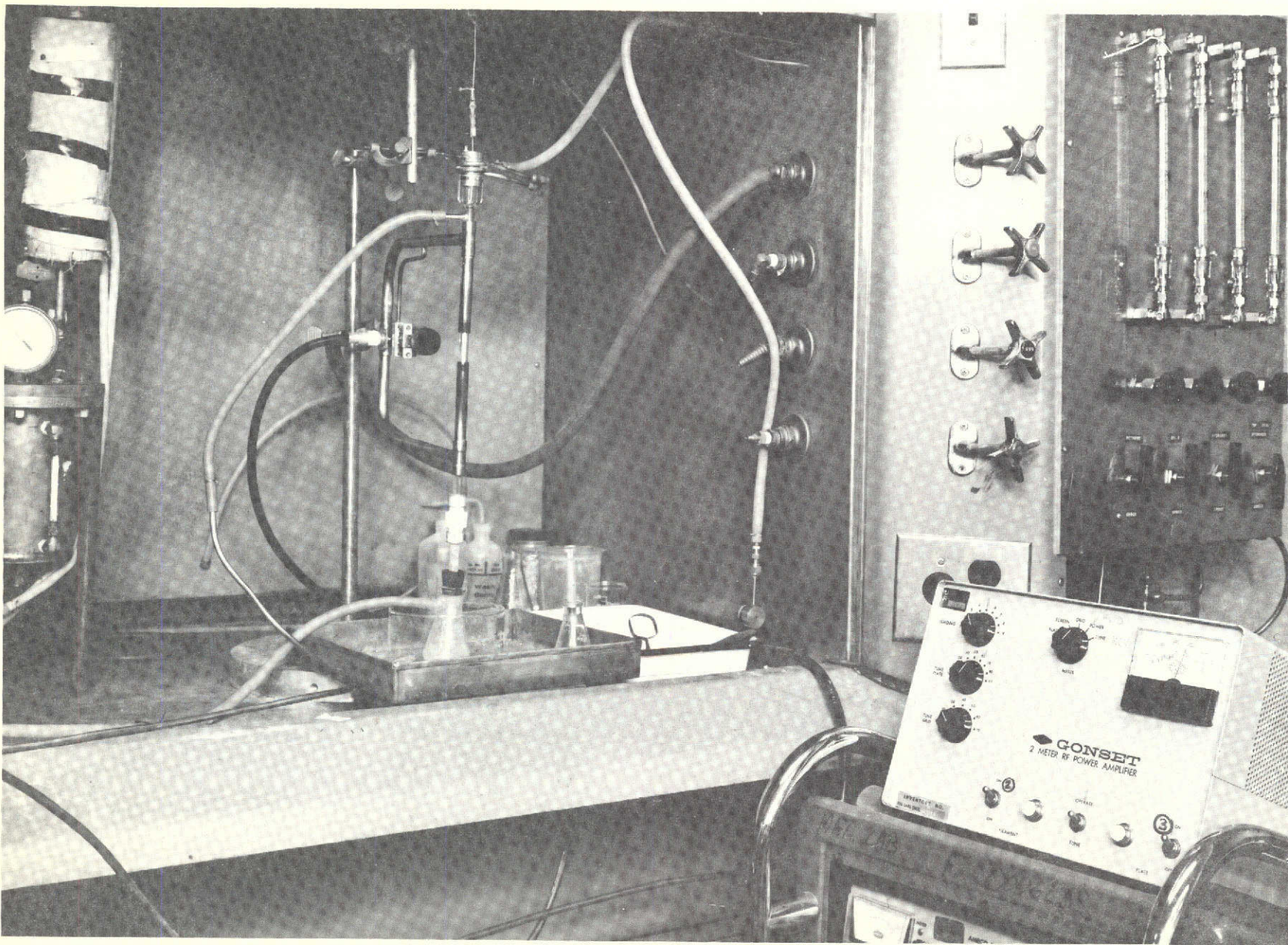
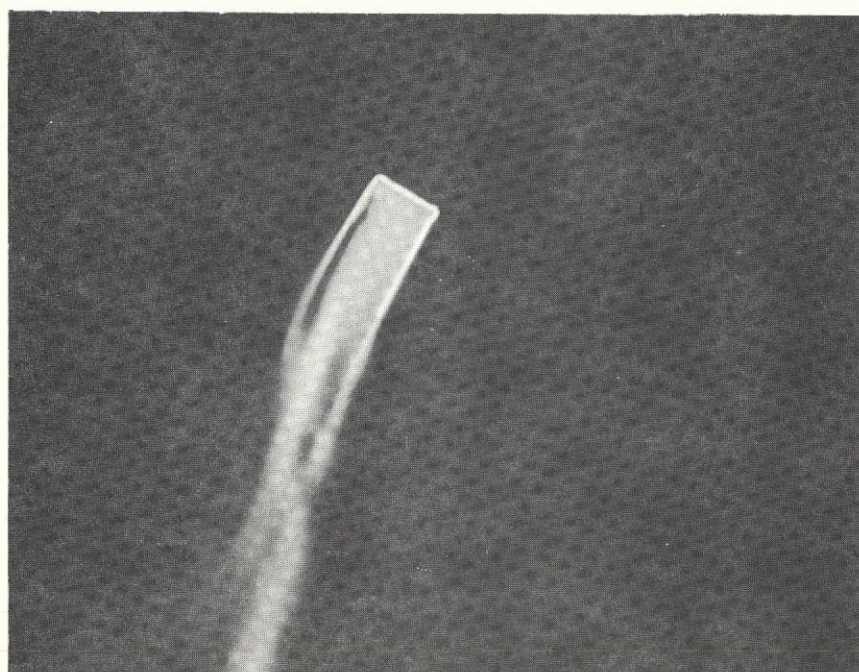
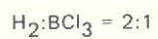


FIG. 18

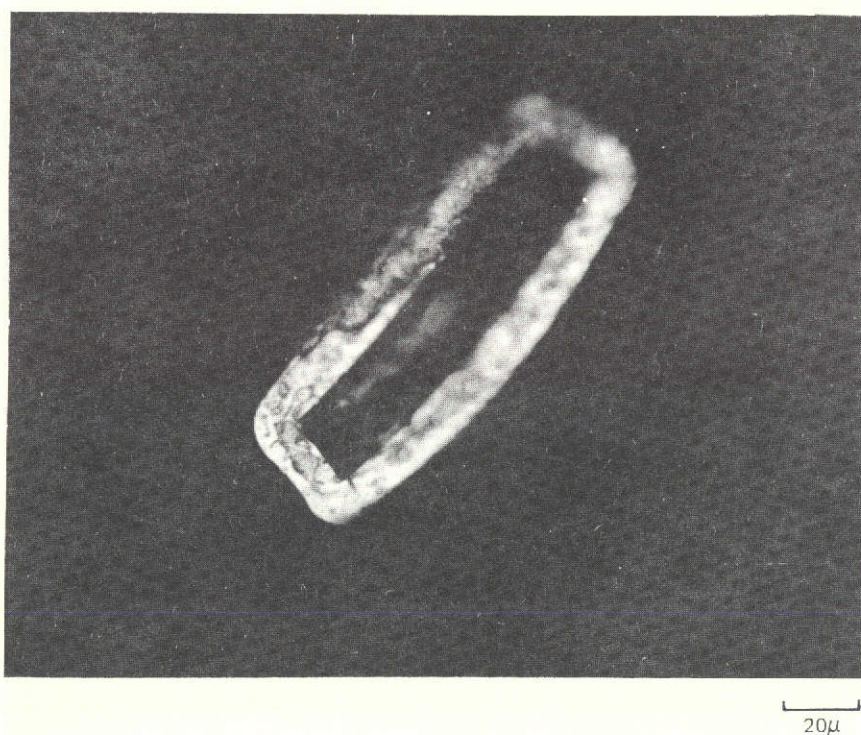
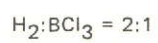
BORON-COATED CARBON TAPE

RF REACTOR — NO PRECOAT ON TAPE

20 μ

BORON-COATED CARBON TAPE

RF REACTOR — GRAPHITE PRECOAT ON TAPE

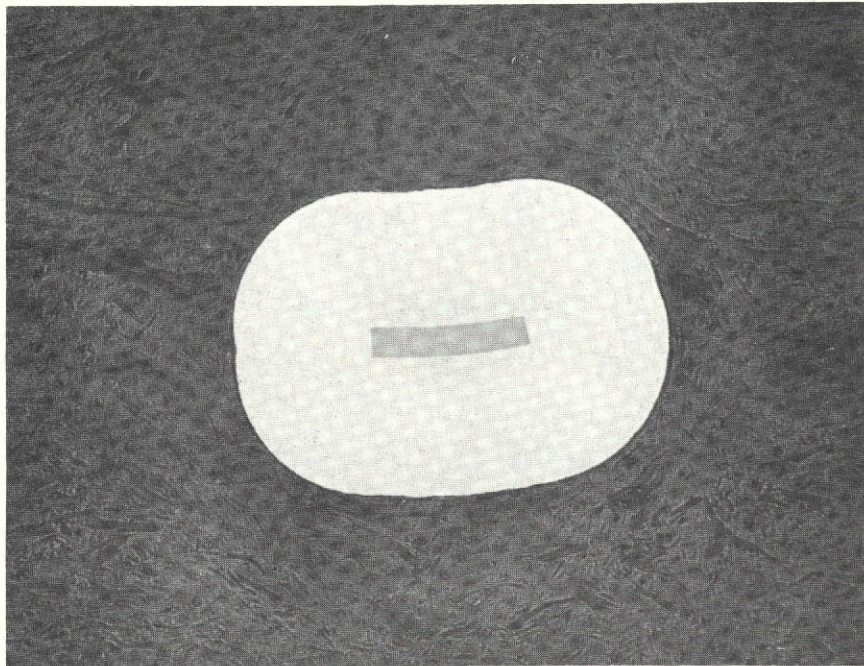


SiC RIBBON ON CARBON SUBSTRATE

SILANE EVAPORATOR AT 10⁰C

37.6 KN/CM² (54.5 KSI) UTS

DC STATIC REACTOR



50 μ

SiC RIBBON ON CARBON SUBSTRATE

SILANE EVAPORATOR AT 3⁰C

71.4 KN/CM² (103.5 KSI) UTS

DC STATIC REACTOR

